# Viscoelastic Properties of Nitrile Rubber Filled with Lignite Fly Ash

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**ABSTRACT:** Nitrile rubber (NBR) compounds containing various loadings of fly ash (FA) were prepared, and their viscoelastic properties and reinforcement mechanism were investigated and compared with those of natural rubber (NR) compounds reported previously. The results obtained exhibit an increase in storage modulus ($G'$) with increasing FA particularly at high FA loading. By contrast, the broadness of linear viscoelastic (LVE) region is found to decrease. With the use of Guth-Gold equation, the positive deviation of experimental values of relative modulus outward the theoretical values is observed at low strain of deformation. However, at high deformation strain, the negative deviation is found. The results imply that the presence of pseudo-network (as formed via FA–FA and FA–NBR interactions) and the ball bearing effect provided by FA having spherical shape are responsible for the reinforcement in FA filled NBR compounds. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 3497–3502, 2010

**Key words:** nitrile rubber; ash; viscoelastic behavior; reinforcement; rheology

## INTRODUCTION

In general, rubber is considered as engineering material for significant parts, for example, seal, automotive industries, conveyor belt, hydraulic industries, and bearing. To improve the mechanical properties, processability, and lower material costs, rubber is always filled with appropriate type of filler. Carbon black and silica are defined as reinforcing filler owing to their small particle size (i.e., large surface area). Because of a large number of silanol groups on silica surfaces, it is found that the formation of filler-rubber network can be formed with functionalized rubbers, such as epoxidized natural rubber (ENR),[1] chloroprene rubber (CR),[2–4] chlorinated polyethylene (CPE),[5–8] and carboxylated nitrile rubber (XNBR).[9]

Fly ash (FA) is a by-product from combustion of coal in thermal power plants. Extracted by mechanical collectors or electrostatic precipitators or combination of both, the disposal of FA makes such a serious environmental problem by contaminating the surrounding atmosphere and taking up space in landfill for its dumping. There are some attempts to decrease the amount of unusable FA, such as mixing FA with cement to achieve high compressive strength concrete[10] and making glass fiber reinforced cement.[11] In addition, the incorporation of FA particles into rubber has been reported to enhance the general shortcomings associated with rubber compounds and vulcanizates including its high shrinkage and low stiffness. Having high silica ($SiO_2$) content of about 40%,[12] FA is considered as semi-reinforcing filler due to the presence of silanol groups on its surfaces leading to an interaction between rubber and FA. So far, most of published works on FA in rubber have focused mainly on cure and mechanical properties of various rubbers including natural rubber (NR),[13–15] nitrile rubber (NBR),[16] styrene butadiene rubber (SBR),[13] and their blends.[17,18] However, there are still a limited number of works concerning rheological properties and reinforcing mechanism of rubber compounds filled with FA. Recently, Saowapark et al.[19] reported on the viscoelastic behavior of NR compounds filled with various loadings of FA. Evidently, there is a phenomenon in which a viscous response is dominant over the elastic response particularly at high FA loading. Such phenomenon is explained by the

spherical shape of FA associated with low FA–NR interaction, promoting molecular slippage under deformation. As a consequence, this work aims to extend the previous work[19] by investigating the viscoelastic behavior in NBR as a polar rubber filled with various loadings of FA. It is hypothesized that the presence of polar group (—CN group) in NBR would interact effectively with silanol group on FA surfaces leading to a formation of transient pseudo-network. This means the magnitude of viscous response domination phenomenon previously found in NR as a nonpolar rubber would be lower in the case of NBR compounds. To exclude the complexity in interaction development in rubber compounds, NBR compounds filled with only FA particles will be prepared and monitored on their viscoelastic properties.

## EXPERIMENTAL

### Materials

NBR (JSR N230) with acrylonitrile content of 35% and Mooney viscosity (ML1+4 at 100°C ) of 56 as a raw rubber was manufactured by Japan Synthetic Rubber Company. FA as filler was supplied by the Mae Moa Power Station of KNR Group Co., Thailand. Characteristic of FA was illustrated in Table I.

### Mixing procedure

NBR compounds were prepared by a 0.5 L internal mixer equipped with Banbury rotors (Chaicharoen Karnchang Co., Thailand). Mixing temperature, rotor speed, and fill factor used were kept constant at 50°C, 40 rpm, and 0.7, respectively. At the beginning, NBR was masticated in mixing chamber for 3 min, and thereafter the first half of FA was charged. It should be noted that the calculation of FA loading was on the basis of parts per hundred of rubber (phr). Mixing was continued for 4 min, and then the other half of FA was added and allowed for further 6 min to achieve good distribution and dispersion of FA in NBR matrix. Finally, the mix was sheeted on cooled two-roll mill (model LRM150, Labtech, Thailand) to obtain compound sheet with thickness of ∼ 5 mm.

### Characterization of FA

The FA particles collected from Mae Moa Power Station was characterized for its chemical composition by the use of the X-ray fluorescence spectrometer (BrukerAXS model S4 Pioneer, Germany). A scanning electron microscope (SEM; LEO 1455 VP, LEO Electron Microscopy, UK) was used to observe morphological characteristic of FA particles with an accelerating voltage of 10 kV. Particle size analyzer

**TABLE I**
**Chemical Composition of FA**

| Compositions | Content (%) | Compositions | Content (%) |
|---|---|---|---|
| $SiO_2$ (silica) | 37.6 | BaO | 0.130 |
| $Al_2O_3$ | 22.4 | SrO | 0.123 |
| CaO | 15.1 | MnO | 0.101 |
| $Fe_2O_3$ | 14.5 | ZnO | 0.0301 |
| $K_2O$ | 2.97 | $ZrO_2$ | 0.0297 |
| $SO_3$ | 2.71 | $Cr_2O_3$ | 0.0240 |
| MgO | 2.29 | $Rb_2O$ | 0.0193 |
| $Na_2O$ | 1.33 | CuO | 0.0187 |
| $TiO_2$ | 0.447 | NiO | 0.0121 |
| $P_2O_5$ | 0.171 | $Y_2O_3$ | 0.00431 |

(Malvern model Mastersizer 2000, UK) was also utilized to measure the FA particle size and its distribution.

### Measurement of viscoelastic properties

Viscoelastic properties of NBR compounds were monitored under oscillatory shear flow using the Rubber Process Analyzer (Alpha Technologies model RPA2000, USA). Initially, the time sweep test was first performed at a constant test frequency and deformation strain of 10 rad/s and 15%, respectively, in order to determine the longest test duration of compounds available without the occurrence of thermal degradation during performing the strain and frequency sweep tests. In the case of strain sweep test, strain of deformation was varied from 0.5% to 1200% at a given angular frequency of 1 rad/s. The frequency sweep test was performed by varying test frequency from 0.5 to 160 rad/s at a constant strain within the linear viscoelastic (LVE) region. All tests were carried out at a given test temperature of 70°C.

## RESULTS AND DISSCUSSION

### Characteristics of FA particles

A determination of FA chemical composition was performed by the use of X-ray fluorescence spectrometer, and the results obtained are shown in Table I. Evidently, the major component found in FA is silicon dioxide ($SiO_2$) or silicate with the amount of 37.6% by weight, followed by some metal oxides-aluminum oxide ($Al_2O_3$), calcium oxide (CaO), and ferric oxide ($Fe_2O_3$). According to a large amount of silica content in FA, the FA has been reported to partly substitute reinforcing carbon black or precipitated silica within the critical loading,[12,13,17] which would result in the rubber vulcanizates having reduced product cost with acceptable mechanical properties. At high FA loadings, FA behaves as a diluent or extender, that is, decreases in both
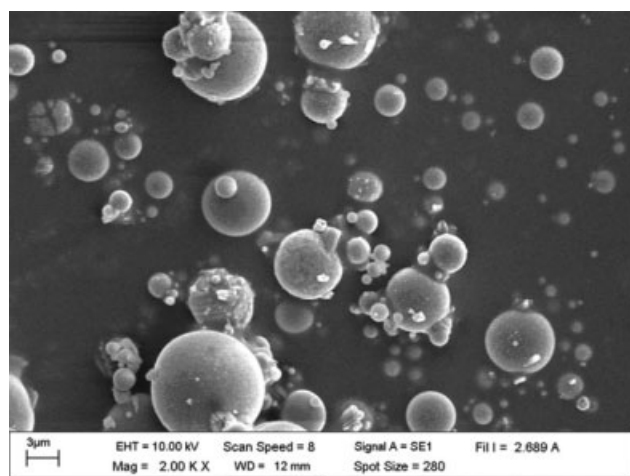
**Figure 1** SEM micrograph of FA particles.[19]



**Figure 3** Time sweep test results of FA filled NBR compounds filled with various FA loadings (strain = 1%; angular frequency = 1 rad/s).

product cost and mechanical strength.[13,16,17] In addition, some metal oxides could promote cure efficiency in NR[13] but shows cure retardation effect in NBR.[16] Furthermore, some trace metals particularly manganese and copper might lead to molecular degradation by acting as oxidizing agent, which in turn affects viscoelastic behavior in NR compounds.[19,20]

Referred to our previous work,[19] Figure 1 exhibits the SEM micrograph of FA particles. Clearly, FA particles are spherical with smooth surfaces. There is no aggregate structure observed unlike the commercially available precipitated silica. Furthermore, the particle size range of FA is from submicron to 200 μ with broad size distribution as illustrated in Figure 2. The reported average particle size of FA is 50.31 μ.

**Viscoelastic behavior**

From our previous investigation on FA in NR,[19] it is found that FA plays strong role on viscoelastic properties of uncured NR as a nonpolar rubber by increasing the viscous response contribution. The combination of ball bearing and molecular degradation effects are proposed to be responsible for such contribution. Thus, in the present study, further investigation of viscoelastic behavior in rubber compounds was carried out by focusing on a NBR, a po-
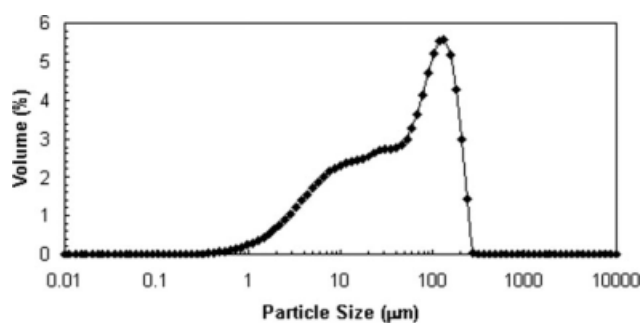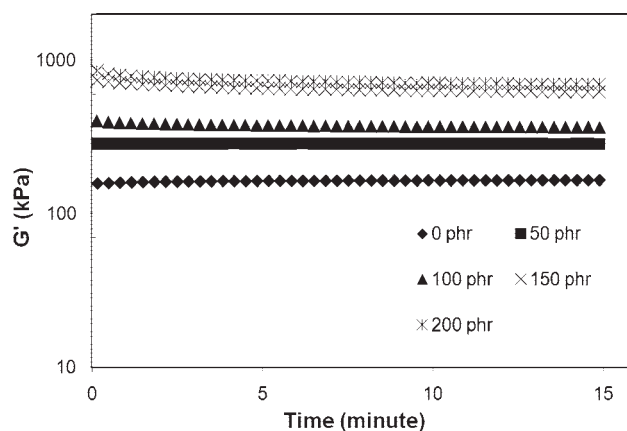


**Figure 2** FA particle size and size distribution.

lar rubber. It is anticipated that the presence of acrylonitrile functional group (ACN) would give significant interaction between silanol groups on FA surfaces and ACN groups on NBR backbone.[21–23] Such interaction might influence the viscoelastic properties of uncured rubber to some extent.

It is, therefore, important to monitor the thermal stability of rubber compounds by performing the time sweep test, so that the longest test duration with no significant thermal degradation could be drawn. By this means, it can be ensured that the results of viscoelastic properties measured are not interfered by the molecular change via thermal degradation of NBR molecules.

As shown in Figure 3, regardless of FA loading, all NBR compounds exhibit no significant change in storage modulus ($G'$) with increasing test duration of 15 min. This implies that all NBR compounds used in this study possess sufficient thermal stability within the test duration that covers the strain and frequency sweep tests. In other words, all results measured under strain and frequency sweep tests illustrated in this work would certainly not interfered by the occurrence of thermal degradation. Additionally, it is noticeable that $G'$ of NBR compounds obviously increases with increasing FA loading.

Figure 4 depicts the viscoelastic response of FA filled compounds performed by the strain sweep test. Obviously, at low strain of deformation, storage or elastic modulus ($G'$) increases with increasing FA loading. A magnitude of increase in $G'$ is more significant at high FA loading particularly at FA loading greater than 100 phr. When compared with carbon black,[24] precipitated silica,[25] and carbon nanotube,[26] FA gives the percolation at higher filler loading. This is due to the relatively small surface area of FA particles available for interacting with rubber molecules. It is also noticeable that the result trends found in this work are similar to those
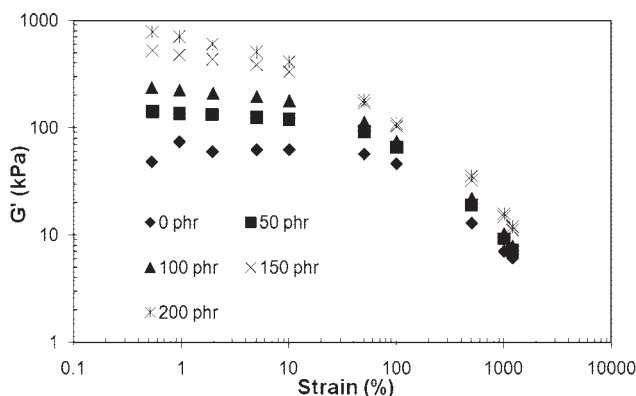
**Figure 4** Logarithmic plots of storage modulus as a function of % strain of NBR compounds filled with various FA loadings measure at a test frequency of 1 rad/s.

observed in CPE filled with precipitated silica (PSi).[5–7] A hydrodynamic effect associated with a filler network formation via strong polymer–silica and silica–silica interactions are reported to be responsible for the results.[5–7] Also, Figure 4 reveals a decrease in width of LVE region, that is, the region with $G'$ independent of strain, with increasing FA loading. This could be explained by the development of a tridimensional transient filler network or pseudo-network particularly at high FA loading. At high deformation strain, such network is disrupted leading to a decrease in $G'$. Additionally, in uncured rubber, a molecular slippage could contribute remarkably to the decrease in molecular entanglement and thus $G'$ at high strain.[6,7,19,27] If the magnitude of discrepancy in $G'$ at low and high strains, generally known as Payne effect,[28] is considered, it is evident that the Payne effect is more pronounced with increasing FA loading, implying the high magnitude of tridimensional transient filler network formation as mentioned previously.

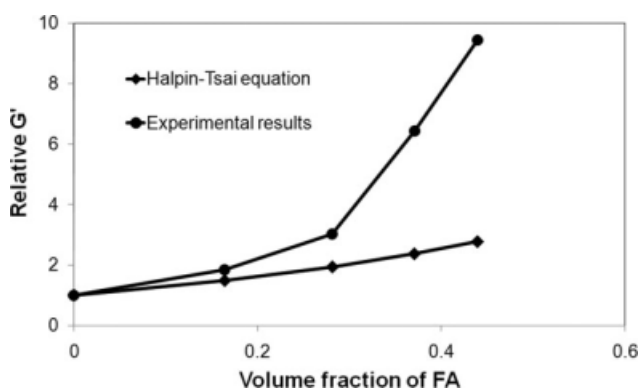Figure 5 shows effects of FA volume fraction on relative $G'$ of NBR compounds at a given shear

strain of 1%, which is still in the LVE region (see also Fig. 4). It is evident that the onset of $G'$ rise is found at the FA loading of 100 phr. In other words, the occurrence of percolation threshold is observed at the FA loading higher than 100 phr. The results support the proposed explanation of the Payne effect caused by the formation of pseudo-network as discussed earlier. Additionally, by applying the Halpin-Tsai equation as shown in eq. (1)[29] to the apparent results, the filler geometrical factor ($\xi$) value of 2 (due to the spherical shape of FA as illustrated in Fig. 1) appears to give the percolation results in line with the experimental data at low filler volume fraction. At further loading, the positive deviation of experimental from the Halpin-Tsai results is observed, which is in good agreement with the percolation threshold as mentioned earlier.

$$E_c/E_m = (1 + \xi\eta\phi)/(1 - \eta\phi) \tag{1}$$

where $E_c$ and $E_m$ refer to Young's modulus of composite and polymer matrix, whereas $\xi$ and $\phi$ represent a geometrical factor of filler and filler volume fraction, respectively.

Figure 6 reveals loss modulus ($G''$) as a function of strain. It can be seen that the result trends are similar to those of $G'$, that is, $G''$ increases with increasing FA loading implying a greater magnitude of tridimensional transient filler network. Also, the LVE region is found to be broadest in the unfilled compound, and appears to decrease with increasing FA loading. The reduction in $G''$ at high strain is believed to be due to the molecular slippage in the case of unfilled compound and to the molecular slippage associated with the disruption of pseudo-network in the case of filled compounds.

When compared with NR, NBR possesses higher polarity, which should theoretically promote the formation of pseudo-network via the dipole–dipole interaction between rubber and filler more
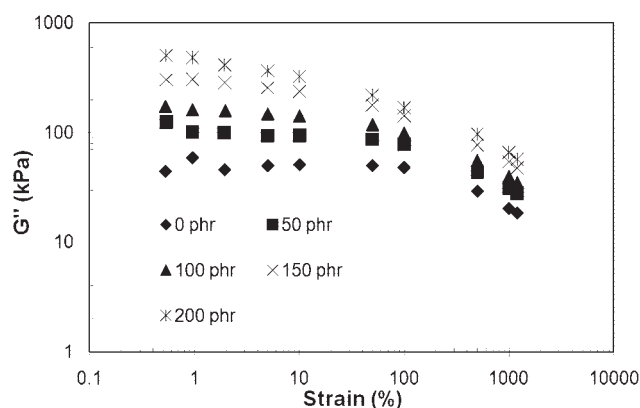


**Figure 5** Comparison of experimental relative storage moduli as a function of FA loading with those calculated from Halpin-Tsai equation (strain = 1%; angular frequency = 1 rad/s).



**Figure 6** Logarithmic plots of loss modulus as a function of % strain at a test frequency of 1 rad/s in NBR compounds filled with various FA loadings.
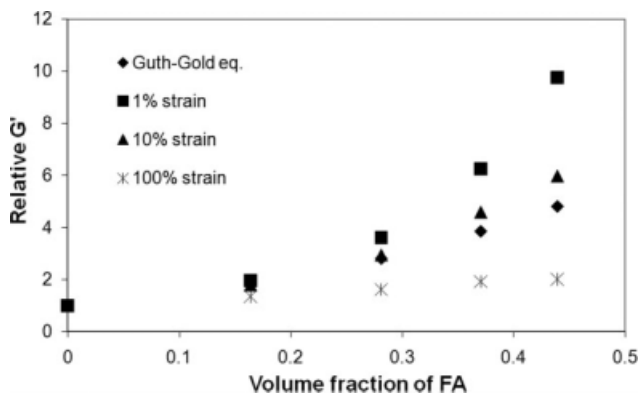
**Figure 7** Theoretical and experimental values of relative storage modulus as a function of FA loading.

efficiently.[21–23] To monitor the magnitude of pseudo-network effect on reinforcing effect, the Guth-Gold equation[30] is used as illustrated in eq. (2). It must be noted that the Guth-Gold equation is applicable at small strain. By substituting the values of filler volume fraction in the Guth-Gold equation, the theoretical values are obtained.[31] According to previous work,[6–8] these relative modulus values are attributed mainly to the hydrodynamic effect at small strain, and any positive deviation from these values at any given of filler volume fraction is reported to be the results of pseudo-network formation.

$$\text{Relative } G' = \frac{G'_{filled}}{G'_{unfilled}} = 1 + 2.5\phi + 14.1\phi^2 \qquad (2)$$

$G'_{filled}$ and $G'_{unfilled}$ are $G'$ of filled and unfilled compounds, respectively.

Figure 7 exhibits a comparison of theoretical values of relative $G'$ calculated from Guth-Gold equation with the experimental values. Evidently, the positive deviation of experimental data at 1% and 10% strain is observed. At 1% strain, the experimental results are much greater than the theoretical values. The positive deviation implies the presence of additional reinforcement provided by the pseudo-network via filler–filler and/or filler–rubber interaction.[6–8] In this system, the development of pseudo-network is believed to be the result of FA–FA particles via H-bond of silanol group and/or FA–NBR interactions via silanol and ACN groups. As strain of deformation is increased to 10%, the experimental results of relative modulus appear to decrease toward the Guth-Gold theoretical results, and the positive deviation from the Guth-Gold results is still observed. However, at high strain of 100%, the negative deviation outward the Guth-Gold results is noticeable similar to the case of NR system filled with FA as reported previously.[19] Saowapark et al. reported a negative deviation of relative modulus measured from the theoretical Guth-Gold results in uncured NR system under deformation strains of 1%, 10%, and

100%. The higher FA loading leads to the greater magnitude of negative deviation, which is attributed to the ball bearing effect. The spherical particles with smooth surfaces of FA particles enhance molecular flow of rubber matrix particularly at FA surfaces. Thus, the high loading of FA leads to the greater molecular flow efficiency, and thus the higher magnitude of negative deviation. Since NR is a nonpolar rubber, the magnitude of pseudo-network via NR–FA interaction is relatively low. In other words, in NR system, the ball bearing effect is dominated over the pseudo-network effect in all deformation strain. On the contrary, in this work where the strong interaction between NBR and FA particles is possible, the pseudo-network development at 1% and 10% strain is dominated over the ball bearing effect. However, as strain is further increased, the transient pseudo-network formed mainly by dipole–dipole and H-bond interactions is disrupted, and the ball bearing effect becomes a key player controlling viscoelastic properties of NBR system.

Figure 8 shows a dependency of $G'$ on test angular frequency in NBR compounds filled with various loadings of FA. It can clearly be seen that $G'$ of all compounds increases with increasing test frequency due to the insufficient time for molecular relaxation of NBR molecules. This would then lead to the increase in degree of molecular entanglement and so elastic contribution. Because $G'$ at low frequency might be used to imply the elastic contribution,[32,33] a greater $G'$ of the compounds shown in Figure 8 means an increase in elastic contribution. The highest $G'$ found in the compound filled with FA loading of 200 phr could be explained by the high magnitude of pseudo-network as mentioned previously. Also, it is noticeable that slopes of the plots (as represented by the straight lines) depend on FA loading, that is, the slope, especially at low frequency, decreases with increasing FA loading, implying a rise in elastic domination degree. In other words, the development of pseudo-network caused by FA
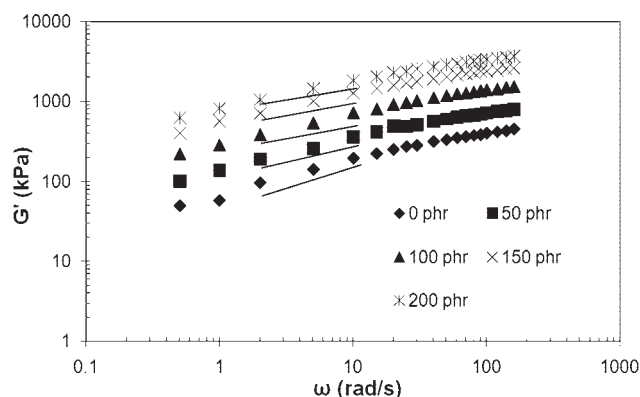


**Figure 8** Storage modulus as a function of frequency at 1% strain of NBR compounds filled with various FA loadings (straight lines represent slopes as an eye-guidance purpose).
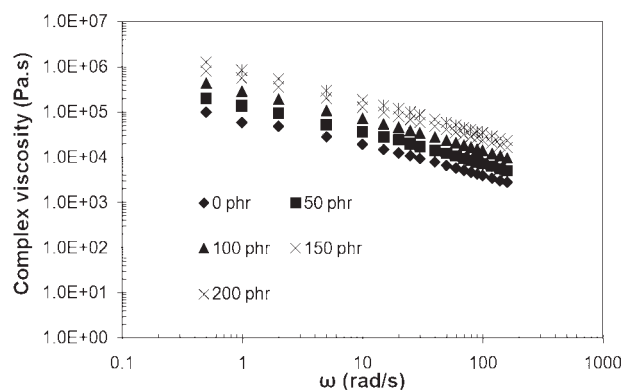
**Figure 9** Complex viscosity of NBR filled with various loadings of FA measured at 1% strain.

particles contributes to a restriction of molecular relaxation.

As illustrated in Figure 9, all NBR compounds show a shear thinning behavior or the so-called pseudoplastic behavior. With high FA loadings, NBR compounds exhibit high complex viscosity due to the extent of molecular restriction provided by hydrodynamic effect and the presence of pseudo-network. However, compared with CPE-based system filled with precipitated silica,[7] FA filled NBR compounds reveal much lower magnitude in complex viscosity rise which is due probably to two main reasons. Initially, the amounts of silanol group and surface area of precipitated silica are much larger than those of FA leading to the smaller magnitude of pseudo-network for rising up the complex viscosity. Then, unlike the precipitated silica having aggregate structure, the spherical shape with smooth surfaces of FA particle could promote molecular flow via the ball bearing effect.

## CONCLUSIONS

In this work, NBR compounds filled with various loadings of fly ah (FA) were prepared, and their viscoelastic properties were monitored under oscillatory shear flow. Reinforcement mechanism was proposed and compared with the NR system filled with FA. Results obtained reveal that with increasing FA loading, storage modulus ($G'$) particularly at low strain increases associated with the reduction in width of LVE region. By comparing with theoretical results of relative modulus calculated from the Guth-Gold equation, it is evident that the reinforcing effect of NBR compound provided by FA particles depends strongly on strain of deformation. At low strain, the high magnitude of reinforcement observed is mainly attributed to the formation of pseudo-network via FA–NBR and FA–FA interactions. However, at high strain, the pseudo-network

is disrupted leading to an increase in molecular flow which is promoted by the ball bearing effect via the spherical shape of FA particles.

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